Formation of an unconventional Ag valence state in Ag$_2$NiO$_2$.

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The Ag ion in the recently synthesized novel material Ag$_2$NiO$_2$ adopts an extremely unusual valency of $\frac{1}{2}$, leaving the Ni ion as 3^+, rather than the expected 2^+. Using first principles calculations, we show that this mysterious subvalent state emerges due to a strong bonding-antibonding interaction between the two Ag layers which drives the lower band beneath the O p complex, eliminating the possibility of a conventional Ag 1^+ valence state. The strong renormalization of the specific heat coefficient, γ, is likely due to strong spin fluctuations that stem from nearly complete compensation of the ferro- (metallic double exchange and the 90° superexchange) and antiferromagnetic (conventional superexchange via Ni-O-Ag-O-Ni path) interactions.

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As with other noble metals, Ag typically adopts a formal valence of 1, 2 or 3 in a compound, corresponding to an empty s-shell and either a full or partially depleted d-shell. Any valence less than 1 would leave the Ag s-shell partially filled and is therefore rather unnatural, particularly with strong oxidizers such as O or F. To our knowledge, there is but one case in which Ag assumes a formal valency of $\frac{1}{2}$: Ag$_2$F [1, 2], and this compound is rather unstable: it decomposes in the presence of water, ultraviolet light, or above 80°C.

Since F^{2-} cannot exist in nature, Ag in Ag$_2$F is perforce $\frac{1}{2}^+$. Ni^{2+}, on the other hand, is a common oxidation state for nickel, just as Ag$^+$ is for silver and one would therefore anticipate that the Ag$_2$NiO$_2$ compound should form, with Ag$^+$ and Ni^{2+} oxidation states, and thus be a magnetic insulator, like NiO. Recently Ag$_2$NiO$_2$, has been synthesized [3], and, intriguingly, did not fit this picture [3, 4]. It remained metallic down to the lowest measured temperatures, with properties rather close to those of delaffosite AgNiO$_2$, a nearly-isostructural compound with one less silver [5]. This has been interpreted as a signal that Ag is underoxidized, or subvalent [Ag$_2$]$^+$, leaving Ni in a 3+ state [3]. In such a case it would indeed be similar to AgNiO$_2$ as well as to better known nickelates, LiNiO$_2$ or NaNiO$_2$, with the low-spin ($t_{2g}^6 e_g^1$) Ni^{3+} being a Jahn-Teller (JT) ion. Not surprisingly then, just as in NaNiO$_2$, a structural transition from a high temperature rhombohedral phase to a (presumably) monoclinic phase was reported in Ag$_2$NiO$_2$ at T_s=260 K [3, 4, 7]. This was attributed in Ref. 4 to a cooperative Jahn-Teller transition of Ni^{3+}, accompanied by orbital ordering (OO), although this attribution was later questioned[6].

This compound poses one principal puzzle: why does Ag assume such an unnatural valence state instead of the expected combination of Ag^{1+} and Ni^{2+}? Additionally, there are unexplained phenomena such as the large electronic specific heat coefficient, $\gamma = 19$ mJ/mole K^2 [4], and the undetermined nature of the magnetic ordering. The layered nickelates and cobaltates, if magnetic, usu-

ally show an A-type antiferromagnetism (AFM) setting in at low temperature. Ag$_2$NiO$_2$ has a Néel temperature of 56 K[3], but the ordering type is unknown, and there are speculations[6] that it is not A-type, but rather AFM in-plane and possibly incommensurate. Unlike most similar materials, the Curie-Weiss temperature changes sign at the structural transition $T_s = 260$ K [3], with the high-temperature undistorted phase showing net FM spin fluctuations ($\Theta = 10$ K), and the low-temperature phase exhibiting AFM ones ($\Theta = -30$ K), both lower than the observed ordering temperature ($|\Theta| < T_N$).

In this Letter we shall demonstrate, using first principles calculations, that most, if not all of these puzzles can be resolved on the one-electron level. The half-valent silver in this compound appears due to the strong bonding-antibonding splitting in the Ag bilayer, pushing most of the bonding Ag-s band below the Ni-d complex and below most of the O-p states. The magnetic disparity with the other layered nickelates and cobaltates can be explained by the fact that hopping between orthogonal O-p orbitals on the same site becomes possible via the metallic Ag layers, thus creating a path for an AFM exchange that compensates the usual metallic FM double exchange and the 90° FM superexchange via oxygen. This compensation leads to strong spin fluctuations which may be responsible for the large specific heat.

The high-temperature crystal structure of Ag$_2$NiO$_2$ is rhombohedral ($R\overline{3}m$), consisting of close packed triangular layers of O-Ni-O-Ag-Ag-O-Ni-O, with edge-sharing NiO$_6$ octahedra. The stacking sequence is ABCABC so that the Ni layers form a BACBAC sequence. For this phase, we used the structural parameters from Ref. [3]. We also performed calculations in the monoclinic ($C2/m$) structure, similar to NaNiO$_2$, suggested by Jansen [7]. We used a full-potential augmented plane-wave with local orbitals (APW+lo) method [9]. To ensure complete convergence we used up to 1024 inequivalent $\mathbf{k}$-points with $RK_{max} = 7$. For magnetic supercell calculations, described in detail later, we used up to 140 $\mathbf{k}$-points in
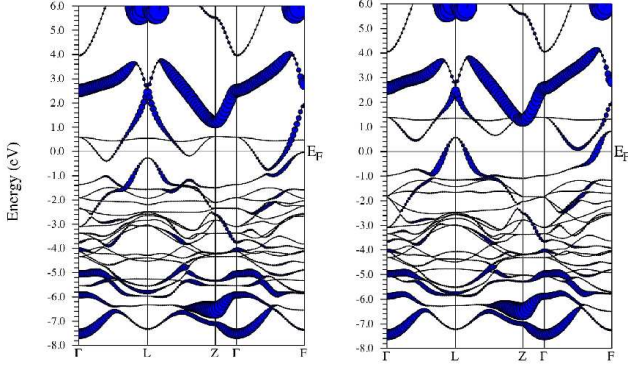
FIG. 1: (color online) LAPW band structure obtained with GGA for minority (left panel) and majority (right panel) spins. Ag$-s$ character is emphasized by fat blue circles.

FIG. 2: (color online) Downfolded LMTO band structure obtained within LDA: NiO (black,solid), Ag-s,p,d (blue, thick) bands. The contribution of Ag-s,p bands is shown as red fatbands.

the (now four times smaller) Brillouin zone and RK_{max} up to 9. Gradient corrections to the exchange correlation potential were included in form of Ref.[10]. The calculated band structure appears to correspond to the $Ag^{0.5+}-Ni^{3+}$ combination, as conjectured by Jensen *et. al.* [3]. To understand the microscopic reasons for such an unusual result, we employed an orbital downfolding procedure as built into the linear muffin-tin orbital (LMTO) method in the atomic spheres approximation (ASA) [8].

We begin by investigating the high-temperature structure with FM ordering. The LAPW bands with the Ag-s character emphasized are shown in Fig. 1. One can see a nearly free electron band starting at ~ -8 eV at the Γ point, then lost in the manifold of the O$-p$ and Ag$-d$ bands between ~ -7 and ~ -2eV, and reappearing above the Fermi level at L and F. Surprisingly, the bottom of this band (at Γ) lies *below* the bottom of the O$-p$ bands (at L). This band originates from the Ag-s and p states, and, since it starts below the O$-p$ states, the valence of Ag, no matter how one chooses to define it, must be less than 1. The obvious question is how can the conductivity band of an s-metal drop below O$-p$ states? To answer this question, we separate the band structure into individual contributions, using the powerful band downfolding technique of the LMTO method.

Fig.2a shows the LMTO bands, obtained for the same structure, but, for simplicity, without spin polarization. We observe that the qualitative character of the LAPW bands, including the relative positions of the Ag and O bands, is reproduced. To understand this band structure, we first remove from the LMTO basis set all states except Ni$-3d$ and O$-2p$. Note that the self-consistent potential for the real compound is still used, so the resulting band structure is *not* the same as for a hypothetical NiO_2 with Ag atom removed. It represents the actual Ni and O states in Ag_2NiO_2, but with the hybridization with other bands switched off. The bottom of the O$-2p$ bands is
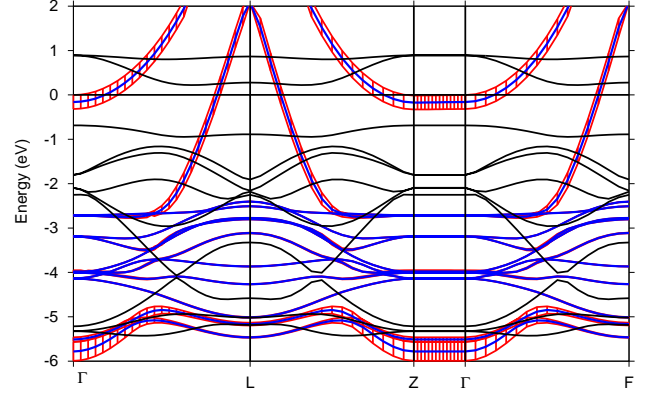
located away from the $\Gamma-$point at ~ -5 eV, and their top overlaps the Ni$-3d$ band around -2 eV. We can also remove Ni$-3d$ and O$-2p$ from the basis, leaving only Ag s,p and d. In this case, we clearly see two bonding and antibonding $sp-$bands that are free-electron-like along in-plane directions (emphasized in Fig. 2 in red). The bonding band intersects the narrow Ag$-d$ bands and finally reappears below the lowest O$-p$ band. The bonding-antibonding splitting is very large, encompassing half the full band dispersion from $\Gamma-$point to the edge of the Brillouin zone. This can be understood from the fact that each Ag has 6 nearest neighbors in its own plane compared to 3 in the neighboring plane.

The bonding-antibonding splitting is the principal feature that distinguishes Ag_2NiO_2 from the similar one-Ag-layer delafossite $AgNiO_2$. The latter behaves more like other $ANiO_2$-based layered materials (A=alkaline) intercalated with a monovalent metal, such as $LiNiO_2$ or $NaNiO_2$. However, even in the delafossite compound, the Ag$-s$ band is considerably lower than the alkaline $s-$bands in $ANiO_2$, such that the very bottom of the s-band drops well below the Fermi level (assuring metalicity), but not below the bottom of the O bands. Obviously, it is the bilayer band splitting in Ag_2NiO_2 that pushes the bonding Ag band down compared to $AgNiO_2$, thus preventing charge transfer from this band to O. Note that in both silver nickelates the bonding Ag band crosses the Fermi level and spans the same energy range as the bands of the NiO_2 complex, thus preventing formation of an insulator even after JT splitting.

The combination of heavy d and light sp electrons in Ag_2NiO_2 should provide interesting transport properties. The Fermi surface (FS) in this compound is comprised of a predominantly Ag$-sp$, cylinder (Fig.3b), with faster electrons in the spin minority channel (in this spin channel Ag_2NiO_2 is a 2D free electron metal) and a central hexagonal cylinder with a surrounding network in the
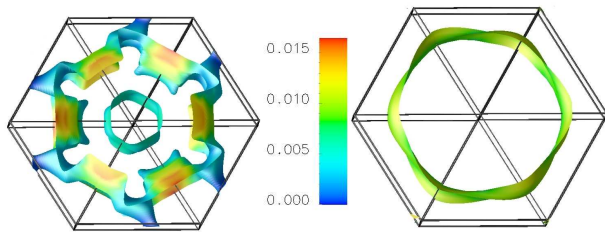
FIG. 3: (Color online) The Fermi surface of Ag_2NiO_2 in the high temperature (rhombohedral) phase in the spin-majority (a) and spin-minority (b) channel, colored according to their Fermi velocity (units are arbitrary).
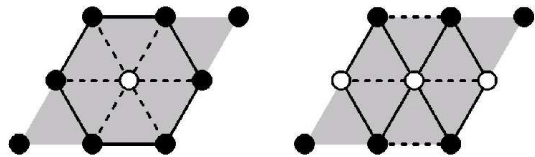

FIG. 4: (Color online) Two of the three (FM not shown) in-plane magnetic configurations investigated in this work. One supercell is shown. Open (filled) circles show spin up (down) sites. The twelve inrreducible bonds (FM and AFM) in each supercell are shown.

TABLE I: The plasma frequencies and density of states at E_F for the high-temperature rhombohedral (R) and low temperature monoclinic (M) structures of Ag_2NiO_2 in the FM configuration.

	$\omega p_x(eV)$	$\omega p_z(eV)$	$N(E_F)(eV^{-1})$
R (up)	2.83	2.58	2.24
R (dn)	2.96	1.12	0.25
M (up)	3.05	2.67	1.32
M (dn)	3.12	3.06	0.27

spin majority channel, formed by hybridized Ni$-d$ and Ag$-sp$ states. The characteristics of the FS in the rhombohedral and monoclinic (to be discussed later) structures are displayed in TableI. Note that the density of states is provided mostly by the Ni bands while conductivity is carried by the Ag bands. The former, though large, is a factor of 3 short of the experimental number (as estimated from the linear specific heat) in the rhombohedral cell and lessens by another a factor of two in the monoclinic cell. One cannot expect an electron-phonon renormalization of this strength and therefore it must be of electronic origin.

Generally, there are two effects of electronic correlation on the band structure. The first is due to the formation of lower and upper Hubbard bands. It can be incorporated in a mean-field way in a method such as LDA+U [12]. However, this can only reduce the DOS at E_F ($N(E_F)$), not enhance it, and in many correlated metallic systems, such as CrO_2, Sr_2RuO_4, or Na_xCoO_2, LDA+U actually worsens the agreement with experiment in terms of magnetic properties or optical transition energies [13]. We carried out LDA+U calculations (in the somewhat simpler LMTO-ASA scheme) and indeed confirmed this conclusion. Curiously, in LDA+U Ag_2NiO_2 remains metallic even with such a U as large as 8 eV. The second effect is a narrowing of the quasiparticle peak near E_F that can be understood as dressing by low-lying bosonic excitations, such as soft spin fluctuations. This effect enhances γ and, generally speaking, depresses the magnetic moment. We shall argue that soft spin fluctuations are indeed operative in Ag_2NiO_2.

The typical magnetic configuration for triangular oxide layers is A-type antiferromagnetism, or ferromagnetically aligned planes stacked antiferromagnetically along the (111) rhombohedral direction. The first surprise is that, contrary to the alkali nickelates, the calculated interplane coupling is ferromagnetic (albeit by only 6 meV), but becomes effectively degenerate (within 0.2 eV) upon the monoclinic JT distortion (a trend we found previously [14] in $NaNiO_2$ where, however, the distortion is much stronger). This can be attributed to competition between the AFM interplane superexchange and metallic FM double exchange. The distortion improves the superexchange paths [14] and slightly suppresses the FM double exchange through loss of DOS at E_F.

Next we consider the intraplane exchange. It has been argued[6] that the in-plane magnetism is itinerant (this could explain why the Curie-Weiss temperature is small compared to T_N) and not FM (possibly incommensurate). To test this computationally, we considered a 2x2x1 supercell (Fig. 4). Using a lowered symmetry to allow for three inequivalent Ni sites, we created three magnetic patterns: $\mathcal{FM}, \mathcal{FI}$ and $\mathcal{AF}$, each supercell containing 12 bonds and four spins. In the $\mathcal{FI}$ pattern half the bonds are AFM and half FM, and three out of four spins are parallel. In the $\mathcal{AF}$ pattern there are two up and two down spins, with 8 AFM and 4 FM bonds. In the nearest neighbor approximation, $E_{\mathcal{AF}}-E_{\mathcal{FI}} = 2J$, where J is the cost of changing one bond from FM to AFM, and $E_{\mathcal{FI}}-E_{\mathcal{FM}} = 6J$. Our calculations give $E_{\mathcal{AF}}-E_{\mathcal{FI}} = 4.1$ meV, and $E_{\mathcal{FI}}-E_{\mathcal{FM}} = 15.0$ meV, consistent with a FM $J = 2.3\pm0.2$ meV. Note however that this number is very small compared to typical triangular-layer nickelates and cobaltates. Moreover, in the rhombohedral structure the last energy difference is reduced from 15 meV to less than 3, a full compensation (within computational accuracy) of FM and AFM in-plane interaction. This can again be traced to the effect of silver. Usually in-plane ferromagnetism is due to 90° superexchange: if two transition metal ions and the bridging oxygen form a right triangle, then the corresponding oxygen orbitals are orthogonal, oxygen-assisted hopping is suppressed, and the Hund's

rule interaction at the O site provides an overall FM exchange (see *e.g.* Ref. 15). The Ni-O-Ni bond angle in Ag_2NiO_2 is indeed close to $90°$, but the metallic Ag bands provide a channel for assisted hopping from one O orbital to another, creating an AFM superexchange path: Ni-O-Ag-O-Ni (a similar mechanism was suggested for $CuGeO_2$ [16]). Competition between the two types of superexchange results in a near compensation for the in-plane exchange, with the net sign depending on details beyond this model[18].

It is clear from the near cancellation of the FM and AFM interaction both in- and out-of-plane that Ag_2NiO_2 is a perfect breeding ground for strong spin fluctuations. The ultimate ordering pattern, then, will depend on fine details of the low-temperature structure. One of the main unanswered questions is whether this structure is JT distorted[7] or not[6]. To address this question computationally we have performed a full structural optimization using a pseudopotential code[17, 19]. This approach has allowed us in the past to establish a tendency to JT distortion in $NaNiO_2$ and $LiNiO_2$[14]. However, optimization in LDA, GGA or LDA+U invariably gave the high-symmetry rhombohedral structure as the ground state. We have verified this result by calculating total energies for the reported rhombohedral and monoclinic structures[7] in LAPW, and again found the former to be lower in energy by 13 meV. While the energy differences involved are too small to definitively eliminate a JT-distorted ground state, our first principles calculations lend support to the Sugiyama *et al* picture[6]. In light of the already substantial disagreement between calculated and measured $N(E_F)$, the loss of nearly half the DOS upon monoclinic distortion also casts doubt on the JT nature of the low temperature phase.

To summarize, we report all-electron, full-potential first principles calculations of the electronic, transport, magnetic and structural properties of the novel exotic material Ag_2NiO_2. We confirm earlier conjectures[3] that the valence state of nickel in this compound is practically Ni^{3+}, while the valence of Ag is very close to $\frac{1}{2}$. The microscopic reason for this unusual configuration appears to be the strong bonding-antibonding splitting in the Ag_2 bilayer, which pushes the bottom of the $Ag-sp$ band below the $O-p$ bands. This results in the rather unexpected $^{3+}$ Ni valence (because of high covalency in spectroscopic measurements this should correspond not to d^7, but rather to d^8L configuration of the ground state, where L is a ligand hole). The Ag bilayer also affects the magnetic properties non-trivially. On one hand, its metallic band provides an additional FM double exchange interaction between the planes, offsetting the standard AFM superexchange, while on the other hand, overlap between the O-p orbitals and the metallic silver layer effectively removes the orthogonality of the O orbitals and revives an AFM superexchange, compensating the usual in-plane ferromagnetism. This creates strongly

fluctuating spins that are responsible, in turn, for a mass renormalization $m^*/m_{band} \approx 3$. Finally, our first principles calculations cannot reproduce the proposed[7] JT distortion, lending some support to the authors[6] who question this suggestion. Overall, the physics of Ag_2NiO_2 appears to be unexpectedly rich and unusual and worth more detailed experimental and theoretical study.

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[18] This effect is even clearer in $AgNiO_2$, where in-plane AFM order is quite strong. Indeed, in $AgNiO_2$ silver sits right on top of an oxygen, providing an easy hopping between two O-p orbitals *via* the same Ag.
[19] We used ultrasoft pseudopotentials with nonlinear core correction (for spin-polarized calculations) taken from www.pwscf.org and Perdew-Bruke-Ernzerhof form of exchange-correlation part in the GGA. The plane-wave

cut-off energy is chosen to be 35 Ry. Structural optimization was performed in variable cell.